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Prebiotic ammonia from reduction of nitrite by iron (II) on the early Earth

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THEORIES for the origin of life require the availability of reduced (or 'fixed') nitrogen-containing compounds, in particular ammonia. In reducing atmospheres, such compounds are readily formed by electrical discharges[1,2], but geochemical evidence suggests that the early Earth had a non-reducing atmosphere[1,3–6], in which discharges would have instead produced NO (refs 7–10). This would have been converted into nitric and nitrous acids and delivered to the early oceans as acid rain[11]. It is known[12–15], however, that Fe(II) was present in the early oceans at much higher concentrations than are found today, and thus the oxidation of Fe(II) to Fe(III) provides a possible means for reducing nitrites and nitrates to ammonia. Here we explore this possibility in a series of experiments which mimic a broad range of prebiotic seawater conditions (the actual conditions on the early Earth remain poorly constrained). We find

**eduction by Fe(II) of nitrites and nitrates to ammonia
 been a significant source of reduced nitrogen on the
th, provided that the ocean pH exceeded 7.3 and is
or temperatures greater than about 25 °C.**

rmine the reactivity of nitrite (NO_2^-) with aqueous olution of both was allowed to react (equation (1)) ormation of ammonia was monitored over time. All ates

$$'e^{2+} + 7\,H^+ + NO_2^- \rightarrow 6\,Fe(III) + 2\,H_2O + NH_3 \qquad (1)$$

here are initial rates. The total amount of ammonia when the reaction was complete, was used to calculate ıtage of nitrite converted to ammonia (the product ammonia concentrations are relative to samples taken t of the experiment. No ammonia is detected in the ' nitrite, nitrate (NO_3^-) or Fe(II).

a in Table 1 confirm earlier observations[16] that Fe(II) e nitrite and nitrate to ammonia. During the reaction, ceeds in the absence of light, the clear pale yellow-tion becomes an optically dense dark-green suspension ric hydroxide ('green rust'). The measured rates are ı those implied in earlier work[16]. In addition to our nitrite reduction reported here, some reduction of ammonia was detected. Ammonia was not, however, producibly from nitrate in every experiment, although elds were ~95% when the reaction occurred. In all nonia formation from nitrate was slower, by at least ' eight, than from nitrite.

conditions that might affect the reaction on the pre-h are not known, the kinetics were studied as a func-perature, pH and concentrations of Fe(II) and nitrite. ıble 1 show the dependence of the rate of reaction on s 1–8). At pH ≤7.3, the reaction does not proceed at le rate. The maximum rate is found at a pH of 7.6. increases above 7.6 the rate falls off, making reactivity H 9 low. The rate also follows Arrhenius behaviour t to temperature (at least between 0 and 40 °C), yield-e of 22,000 K^{-1}. Data in Table 2 show that the rate roportion to the concentration of nitrite but in a more nanner with the concentration of Fe(II). A least-of the equation $y = kx^n$ to the data on rate as a func-$^{2+}$] yields a value of 1.8 for n, thus giving an apparent t pH 7.9) of the form rate $= k[NO_2^-][Fe^{2+}]^{1.8}$, where $^{-6}$ min^{-1} $M^{-1.8}$.

eriments described were conducted in solutions that e from pure water. The ocean today contains large amounts of sodium chloride as well as small amounts of other ions, including K^+, Mg^{2+}, Ca^{2+}, Br^- and SO_4^{2-}. The presence of these salts in the early ocean may have affected the kinetics of nitrite reduction. Anions may interfere with the reaction, particularly by binding to the Fe(II) centres and deactivating them. Cations may complex nitrite or anionic iron complexes. Increased pressure of carbon dioxide would have lead to increased bicarbonate concentrations, and the concentration of sulphate is likely to have been lower than it is today[13]. The concentration of halide ions in the early ocean is not well known, but indications are that it was not far from the current value[12].

When 0.53 M NaCl is added to the reaction, a fivefold increase in the rate is observed (entries 6 and 7, Table 1). When other cations (that exist in sea water now) are added, an additional rate increase is observed (entries 7 and 9). The presence of sulphate and bromide ions at levels equal to those found in present-day environments reduced the rate of reduction slightly (entries 7 and 10). The situation with bicarbonate is more complicated. The carbon dioxide pressure (and carbonate/bicarbonate concentration) was likely to have been much higher in the early atmosphere than it is today, with suggested values ranging from 0.2–10 atm[3,6,17]. Reactions in this range are difficult to run because the limited solubility of siderite ($FeCO_3$) required very low concentrations of Fe(II). Two experiments were conducted in solutions that had been saturated with sodium bicarbonate, one at 25 °C and one at 80 °C (entries 16 and 17). At the end of two months the room-temperature experiment showed no production of ammonia. In the 80 °C experiment, however, nitrite was reduced at a rate of 0.006 μM min^{-1}. If we correct for temperature (using the Arrhenius equation) and the concentration of Fe(II), this rate is what would be expected, within experimental error, from the rate law given previously.

TABLE 1 Rate of reduction of nitrite to ammonia by aqueous Fe(II)*

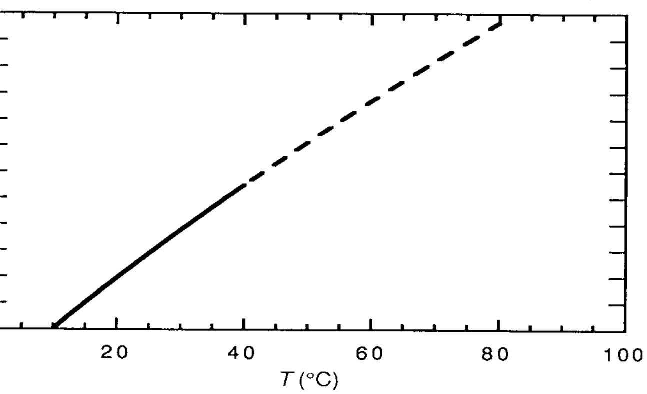
Entry	T (°C)	pH	Additions†	Rate (μM min^{-1})	Prod. yield‡(%)
1	22	7.1	None	<0.004§	—
2	22	7.3	None	<0.008§	—
3	22	7.5	None	10	35
4	22	7.6	None	15	37
5	22	7.9	None	8.8	28
6	22	8.0	None	8.5	33
7	22	8.0	NaCl	44	64
8	22	8.4	NaCl	6.6	25
9	22	8.0	Cations	67	85
10	22	8.0	Anions	36	52
11	0	7.6	None	~0.1	3.8
12	11	7.6	None	0.45	24
13	23	7.6	None	12	44
14	30	7.6	None	61	74
15	40	7.6	None	630	60
16	22	7.5	CO_2	0	0
17	80	7.5	CO_2	0.006	75

* A volume of a nitrogen-purged $NaNO_2$ solution (23 mM) sufficient to make up a 0.32 mM solution was added by syringe to a 12.3 mM $FeCl_2$ (Aldrich) solution (350 ml) stirred under nitrogen purging. In occasional experiments a volume of $FeCl_2$ solution sufficient to make up 12.3 mM was added to a 0.32 mM solution of $NaNO_2$ with no change in results. After a ($t = 0$) blank was withdrawn and purging stopped (to avoid sweeping out ammonia), the reaction was allowed to proceed under nitrogen. Aliquots were withdrawn by syringe and analysed for ammonia by colorimetric methods[14].

† Concentrations: NaCl, 0.53 M NaCl; anions, 5 mM NaBr, 28 mM Na_2SO_4 and 0.53 M NaCl; cations, 51 mM $MgCl_2$, 12 mM $CaCl_2$, 13 mM KCl and 0.53 M NaCl; CO_2, saturated with respect to $FeCO_3$, 1 atm CO_2, and 0.53 M NaCl.

‡ The percentage of reacted nitrite that is converted to ammonia.

§ These values are within experimental noise and represent upper limits. All other numbers and changes from experiment to experiment are significant.



of the pseudo-first-order rate constant ($k' = k[Fe(II)]^{1.8}$) as a ocean temperature (pH 7.6, 0.2 atm CO_2, saturated with derite). The rate constant k was measured experimentally nd 40 °C (solid line) and extrapolated to 80 °C (dashed line); es for the K_{sp} (solubility product) of $Fe(CO_3)$ are from ref. 22.

ese data we can calculate a possible rate of ammonia in the early ocean. Shock heating produces NO (ref. ance by equation (2):

$$CO_2 + 1/2\ N_2 \rightarrow NO + CO \quad (2)$$

a production rate for NO of 1.1×10^{11} mol yr^{-1} from ting by meteors passing through the atmosphere o (see ref. 9 and refs therein). To calculate the producf NO from lightning, we have taken the most recent f lightning frequency[18], together with an estimate of ncy with which NO is produced from lightning , to obtain 1.4×10^{11} mol yr^{-1}. Next, we assume that is washed into the ocean[11]. Depending on the stoichihe reactions involved, 20–50% of the NO is converted ,19,20. Choosing an intermediate value of 33%, we itrite production rate of 4.9×10^{10} mol yr^{-1}. We will ocean at 25 °C, under 0.2 atm of carbon dioxide, at is would limit the concentration of Fe(II) to 190 nM, siderite solubility from equilibrium constants[21] and amic data for $FeCO_3$ (ref. 22). Under these condiassuming a steady state between atmospheric producite and its reduction to ammonia, the rate of reduction ugh to hold the concentration of nitrite to 1.6 μM. tion rate shows a strong dependence on temperature. temperature the solubility of siderite increases[22] uld also depend inversely on [CO_3^{2-}]). If the concen-Fe(II) is fixed by the solubility of $FeCO_3$, then we can eudo-first-order rate law, rate $= k'[NO_2^-]$, where $k' =$. A plot of k' against temperature (at a partial CO_2 of 0.2 atm.) is shown in Fig. 1. For this plot, tificially held the pH at 7.6 to separate the effects of e and pH on k'. Between 10 and 80 °C, the rate of ction in the ocean increases by 11 orders of magnily, reduction is strongly favoured by warm environexample at 80 °C, the steady-state concentration of ps to 4.1×10^{-15} M.

sible sink for nitrite, competing with reduction to s destruction in waters passing through oceanic hydsystems. At present, the timescale for ocean cycling ese systems is ~10 million years[23], but we adopt a ation to take into account increased tectonic and/or tivity early on[24,25]. The fate of nitrite in hydrothermal not known. If we assume complete destruction to a worst-case model, and if the oceans cycled through ermal systems every 2.5 million years, the maximum al sink for nitrite would be $\sim 3 \times 10^{8}$ mol yr^{-1}. This al sink is a factor of 150 smaller than nitrite reducbulk ocean at an ocean temperature of 25 °C; at an erature of 80 °C, it is a factor of 3×10^{10} lower.

competing abiotic sink for nitrite is aqueous photostruction in near-surface ocean waters. It is difficult e importance of this sink. The amount of near-ultrareaching the ocean surface in the prebiotic environertain[26]. One product of photolysis is NO, which can atmosphere and be reconverted to nitrite/nitrate. e water, there is no net reaction because the primary cts (NO and OH^-) back-react to reform nitrite with ncy[27]. Net photochemical destruction in the ocean is on the presence of poorly defined trace species[27], almost certainly present at different concentrations completely) in the early Archaean ocean. We can emical rates occurring in the contemporary ocean[27] n upper limit to the size of the photochemical sink. s 1,200 times higher than nitrite reduction at room , but a factor of 1.2×10^{5} lower at 80 °C. Again, nperatures strongly favour reduction to ammonia. modern oceanic vertical mixing rate of 3 m yr^{-1} (ref. nmonia, iron and nitrite concentrations would have uniform over the whole ocean.

y-state concentration of ammonia (present mostly

TABLE 2 Dependence of the rate of nitrite reduction by aqueous Fe^{2+} on nitrite and Fe(II) concentration*

[NO_2^-] (mM)	[Fe^{2+}] (mM)	Rate (μM min^{-1})	pH	Relative concentration	Relative rate	Product yield† (%)
Nitrate concentration dependence						
0.0327	12.3	0.9	7.9	1	1	—
0.131	12.3	5.0	7.9	4	5.6	34
0.327	12.3	8.8	7.9	10	9.8	28
0.654	12.3	18	7.9	20	20.0	30
0.327	12.3	4.2	8.0	1	1	28
0.654	12.3	7.8	8.0	2	1.9	26
Fe(II) concentration dependence						
0.327	3.2	1.3	7.9	1	1	—
0.327	4.9	1.3	7.9	1.5	1	27
0.327	8.9	7.7	7.9	2.8	6.1	30
0.327	12.3	8.8	7.9	4	6.9	28
0.327	19.7	27	7.9	6.2	21	42

* Values are measured room temperature. Variable volumes of nitrogen-purged 23 mM $NaNO_2$ (Baker) were added by syringe to an $FeCl_2$ 12.3 mM; (Aldrich) solution (350 ml) stirred under nitrogen purging. After a ($t = 0$) blank was withdrawn and purging stopped (to avoid sweeping out ammonia), the reaction was allowed to proceed under nitrogen. Aliquots were withdrawn by syringe and analysed for ammonia by colorimetric methods[14].

† The precentage of reacted nitrite that is converted to ammonia.

as ammonium, NH_4^+) would depend on what sinks for ammonia were active. Again we assume an ocean temperature of 25 °C and a pH of 7.6. If the predominant sink for ammonia was hydrothermal decomposition (such as was outlined for nitrite decomposition above) then, with a production rate of 3.6×10^{10} mol yr^{-1}, the steady-state ammonia concentration would have been 70 μM.

An alternative sink is gas-phase photochemical destruction of ammonia in the atmosphere, as modelled by Kasting[29]. We assume ammonia in the ocean to be in equilibrium with ammonia in the atmosphere. In this case, the steady-state concentration of ammonium ions in the ocean would have been 3.6 μM. If other sinks were active, this value would be lower. Although sequestration in clays represents a possible sink, there is reason to believe that this process would only have set an upper limit of 0.01 M on the NH_4^+ concentration[30].

The reduction of nitrite to ammonia represents a plausible process if oceanic pHs were greater than 7.3. The reaction is also strongly favoured by warmer oceans[17,31,32]. Whether ammonia concentrations of the order of 3.6–70 μM in the ocean would have been adequate for prebiotic evolution remains uncertain[2]. □

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